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HELIUM PUMPING BY 4.2°K CRYODEPOSITS



J. D. Haygood and R. Dawbarn

ARO, Inc.

January 1967

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FOREWORD

The research reported herein was sponsored by Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), Arnold Air Force Station, Tennessee, under Program Element 65402234.

The results of the research were obtained by ARO, Inc. (a subsidiary of Sverdrup & Parcel and Associates, Inc.), contract operator of AEDC, under Contract AF 40(600)-1200. The research was conducted from February to July, 1966, under ARO Project Nos. SW3417 and SM3415-M38. The manuscript was submitted for publication on September 20, 1966.

This technical report has been reviewed and is approved.

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ABSTRACT

Studies of the trapping of helium by condensing argon on a 4.2°K surface have indicated that this is an effective method of removing helium from vacuum systems. Pumping speeds as high as 18.3 liters/sec-cm² for 77°K helium (converted to 300°K helium) were obtained. Exploratory tests of nitrogen and oxygen as substrate gases for helium sorption were also carried out. During these tests the capture coefficients of argon, nitrogen, and oxygen were measured and found to be near one.

CONTENTS

	<u>Page</u>
ABSTRACT.	iii
NOMENCLATURE.	vi
I. INTRODUCTION	1
II. APPARATUS	1
III. PROCEDURE.	3
IV. CALIBRATION	4
V. EXPERIMENTAL RESULTS	7
VI. DISCUSSION	8
VII. CONCLUSIONS	14
REFERENCES	15

TABLE

I. Results of Steady-State Sorption Tests.	9
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APPENDIXES

I. Illustrations

Figure

1. UHV Chamber	19
2. Gas Addition System	20
3. Typical Pumpdown Curve	21
4. Pumping Speed versus Pressure Ratio	22
5. Pressure History during an Isotherm Test	23
6. Helium/Argon Pressure Isotherm	24
7. Helium Isotherm versus Mole Ratio Helium/Argon.	25
II. Methods of Calculations.	29

NOMENCLATURE

K_{O_2}	Conductance of orifice in shroud (subscript is gas species), liters/sec
k_{He}	Conductance of leak (subscript is gas species), liters/sec
M	Molecular weight
$M. S.$	Partial pressure inside shroud (mass spectrometer), torr
N	Number of molecules
n	Number of moles
P_c	Chamber pressure inside shroud (ion gage), torr
P_f	Forepressure on leaks, torr
P_o	Chamber pressure outside shroud (ion gage), torr
Q	Volumetric flow rate, liters/sec
R	Universal gas constant, ergs/mole-°K
T	Temperature
T_s	Shroud temperature, °K
t	Time, sec
V_c	Volume of vacuum chamber, liters
V_f	Measured volume in leak system (surge tank), liters
ξ	Outgassing, torr-liters/sec
σ_c	Gage factor (ion gage inside shroud), torr/division
σ_{ms}	Gage factor (mass spectrometer), torr/division
σ_o	Gage factor (ion gage outside shroud), torr/division

SUBSCRIPTS

a	Adsorption
v	Vaporization

SECTION I INTRODUCTION

Designers of proposed space laboratories, whether of the expandable structure type or prefabricated modules to be assembled in orbit, all hope to provide a shirt-sleeve environment for the scientists in space. One of the more promising atmospheres in such a space laboratory appears to be a mixture of helium (He) and oxygen (O₂) (Ref. 1). The anticipated leak rates of such structures will result in a sizable gas load of each of these gases in any environmental chamber used to test them. Since simultaneous testing of the reflectivity of temperature control surfaces on the outside of such structures requires a clean chamber, free from any oil contamination, an alternative to the conventional diffusion pump is desirable.

The O₂ could be pumped effectively by 20°K cryopanel (Ref. 2); however, the few alternative methods of pumping He are inefficient. Ion (or sublimation) pumping at present is limited to speeds on the order of from 10 to 50 liters/sec for commercially available pumps. Molecular sieves promise better pumping speeds, but they are sensitive to contamination by other gases and have a limited capacity.

From theoretical considerations, further discussed in Section VI, an experimental investigation of the trapping of He in 4.2°K cryodeposits was initiated. This investigation has shown that the trapping* of He by condensing argon (Ar) on a 4.2°K surface offers an alternative to the diffusion pump. A cursory examination of trapping by O₂ and nitrogen (N₂) indicates that they, too, may be effective for pumping He.

SECTION II APPARATUS

The chamber used in this study is shown in Fig. 1 (Appendix I). It consists essentially of a 36- by 30-in. vacuum chamber containing a 7-in.-diam spherical cryosurface and two independent gas addition systems. The vacuum chamber is constructed of stainless steel, all heliarc

*Removal of a noncondensable gas either by sorption or physical encapsulation within a condensing gas.

welded. A 25- by 24-in. inner shroud of 1/8-in. copper can be cooled by circulating liquid nitrogen (LN₂) through tubing welded to its outer surfaces. The cryosphere is centrally located inside the shroud, and its fill and vent lines are vacuum jacketed and shielded inside the chamber. The surface area of the sphere available for pumping is 970 cm².

The gas addition systems (Fig. 2) are similar, each consisting of a surge tank, a pressure gage for measuring the forepressure of the gas, and a series of sintered stainless steel leaks arranged in parallel (Ref. 3). Each gas addition system has an independent pumping station.

A thin-walled circular orifice in the bottom of the shroud provides a convenient method for frequent in-place calibration of the gages and mass spectrometer (see Section 4.2). The pressure in the working volume of the chamber is monitored by an ion gage and a mass spectrometer. Tubulation inside the chamber prevents the gages from directly sensing molecules from either the cryosurface or the calibration orifice. The time constant of the tubulation is calculated as 8.6×10^{-4} sec for Ar at 77°K, and thus the gage response is much faster than any pressure changes to be followed in these experiments. A second ion gage, located on the outside wall of the chamber, is used to read the pressure in the annular region between the chamber and the shroud.

The vacuum chamber pumping system consists of a 6-in. oil diffusion pump with an LN₂ baffle. The diffusion pump is backed by a mechanical roughing pump. The chamber can be isolated from the pumping system by a 6-in., high vacuum, gate valve. The entire vacuum system is equipped with outgassing heaters capable of producing temperatures up to 500°K.

The cryosphere was plumbed directly to an He liquefier (250-w cryostat) via a superinsulated, vacuum jacketed transfer line. For the latter portion of this study the He boiloff from the sphere was returned via a copper tube helically wrapped around the liquid Helium (LHe) transfer line to reduce the radiation load across the vacuum jacket. The complete assembly was encased in Styrofoam® insulation. An adjustable needle valve located in the cryostat was used to set the LHe flow. Temperatures in the sphere were indicated by an He vapor pressure thermometer (centered in the cryosphere), and the LHe level was monitored by a germanium thermistor located in the exhaust line.

SECTION III PROCEDURE

The LN₂ was turned on to the shroud 24 hr before a series of experimental runs was to be made to allow temperatures to stabilize and to pre-cool the cryosphere to 77°K. The base pressures in the chamber were measured by the ion gages, and a background scan was made with the mass spectrometer. Prior to a series of tests the gages and mass spectrometer were calibrated for the gases to be used, as outlined in Section IV.

The chamber was isolated from the pumping system by closing the gate valve, and LHe was transferred to the cryosphere. When the germanium thermistor indicated that the sphere was full, the needle valve in the cryostat was adjusted to maintain a slow transfer of liquid, sufficient to maintain the liquid level as indicated by the thermistor.

3.1 EVALUATION OF HELIUM TRAPPING BY THE PUMPDOWN METHOD

Pumpdown tests were used for rapid, qualitative evaluation of the relative pumping capabilities of N₂, O₂, and Ar. With the main pumps closed off by the gate valve, gaseous helium (GHe) was admitted to the chamber via the leak system until the mass spectrometer reached the desired reading. The GHe was turned off and the test gas (O₂, N₂, or Ar) was admitted at a known rate. The resulting pumpdown curve of the GHe was recorded on the mass spectrometer readout recorder. The partial pressure of the test gas (O₂, N₂, or Ar), during its addition, was used as a measure of its capture coefficient.* From comparisons of the pumpdown curves and other considerations it was determined that Ar would be the best trapping gas for further study.

3.2 SIMULTANEOUS GAS ADDITION METHOD

The second phase of the testing was to determine the effective He pumping speed for simultaneous He and Ar flows. Quantitative measurements of the trapping of He by Ar were carried out by the steady-state method. Argon and helium were admitted to the chamber simultaneously. After times ranging from 10 to 45 min, a constant He partial pressure was obtained. The criterion of steady-state conditions was a constant

*Ratio of the measured pumping speed to the calculated maximum pumping speed.

pressure reading for 5 min. To minimize transient effects the system was pumped through the orifice during these runs. Thus, the pumping speeds obtained represent the sum of the orifice and cryosurface pumping speeds.

3.3 DETERMINATION OF SORPTION ISOTHERMS

It was suspected that repeated runs made over previous cryodeposits might be influenced by the past history of the surface. Therefore, an attempt was made to examine more closely the sorption process. This involved laying down a known amount of Ar cryodeposit and then admitting known amounts of He.

With the chamber pumping system valved off, the Ar was admitted to the chamber at a known rate for a measured time. The steady-state pressure in the chamber during this time was recorded by the gages. These data also provided information to calculate the capture coefficient of Ar on the 4.2°K surface.

After coating the surface, the Ar inlet was closed. The He leak system valve was then opened and GHe was allowed to enter the chamber at a known rate for 5 min. The He was turned off and a constant pressure was soon reached and recorded. A series of additions was made, and the corresponding constant pressures were recorded. These data were used to plot isotherms for the particular Ar deposit. The He pressure during the initial addition of He was used to calculate the capture coefficient of He on pure Ar for each Ar deposit thickness.

SECTION IV CALIBRATION

4.1 LEAKS

Each leak was calibrated for the gases used by recording the pressure drop in a known volume as the gas flowed from this volume through the leak into the vacuum chamber (Ref. 3). Consider two volumes at pressures P_f and P_c , respectively, connected by a small leak with a conductance k . The resulting gas flow through the leak may be expressed as

$$V_f \frac{dP_f}{dt} = k (P_f - P_c)$$

If the pressure P_c is kept much lower than P_f by a pumping system, then the expression may be written

$$V_f \frac{dP_f}{dt} = k P_f$$

(since $P_f \gg P_c$)

and

$$\frac{dP_f}{P_f} = \frac{k}{V_f} dt$$

Integration yields

$$\ln P_f = \frac{k}{V_f} t + \ln C$$

Using the initial conditions $t = 0$, $P_f = P_i$, then

$$\ln \frac{P_f}{P_i} = \frac{kt}{V_f}$$

Thus the conductance of the leak is given by

$$k = \frac{V_f}{t} \ln \frac{P_f}{P_i}$$

The known volume, V_f , was measured by filling the components of the system with alcohol and measuring each volume during assembly. The pressure-time response was measured with a calibrated pressure transducer.

4.2 PUMP ORIFICE AND GAGE CALIBRATION

The vacuum system was pumped down with the diffusion pump, and the shroud was cooled to 77°K. The base pressure was measured by the ion gages. The pump was then closed off with the 6-in. gate valve, and the rate of rise caused by outgassing was recorded.

Using a previously calibrated leak, He was admitted to the chamber at a known rate. With the gate valve open, the He was pumped from the chamber via the orifice, and the steady-state pressures from both ion gages were recorded. The gate valve was then closed and the rate of rise of the pressure in the chamber for this same inflow rate was noted. This procedure was repeated with increasing He flows until all scale ranges of the ion gages had been covered, with at least three data points on each scale.

The accumulated data were used in the following analysis to determine the gage sensitivity factors and the conductance of the orifice.

Although the conductance of the orifice could be calculated, it was also measured experimentally to check the consistency of the equations, the applicability of kinetic theory, and the gage calibrations. The calculated value of the He conductance using the Clausing factor (Ref. 4) was 100.0 liters/sec. The experimentally determined value was 102 liters/sec with a scatter of less than 5 percent. This agreement indicates that the experimental error in calibration does not exceed 5 percent.

4.2.1 Gage Calibration

From the ideal gas law,

$$P \frac{dV}{dt} + V \frac{dP}{dt} = \frac{dn}{dt} RT$$

where n is the number of moles.

The gas flowing into the chamber may be considered as the sum of that through the leak Q_1 plus an outgassing load ζ . Therefore,

$$P \frac{dV}{dt} + V \frac{dP}{dt} = Q_1 + \zeta \quad (1)$$

With the main gate valve closed,

$$\frac{dV}{dt} = 0$$

and

$$\frac{dP}{dt} = \frac{Q_1 + \zeta}{V}$$

Assuming a constant outgassing rate, it can be shown that

$$\sigma_{on} \dot{P}_{on} = \sigma_{cn} \dot{P}_{cn} = \frac{P_f k + \zeta}{V_c} \quad (2)$$

Where the subscript (cn) refers to the c gage on the n scale, and the subscript (on) refers to the o gage on the n scale.

Thus

$$\frac{\dot{P}_{on}}{\dot{P}_{cn}} = \frac{\sigma_{cn}}{\sigma_{on}} \quad (3)$$

giving a ratio of gage factors. From Eq. (2)

$$\dot{P}_{cn} = \frac{k}{\sigma_{cn} V_c} P_f + \frac{\zeta}{\sigma_{cn} V_c} \quad (4)$$

Therefore, plotting \dot{P}_{cn} versus P_f yields a straight line when outgassing is either constant or negligible. The volume V_c was determined during assembly of the chamber by measuring components and calculating the

resultant volume. The values of σ_{cn} were determined by the slope of the straight line from Eq. (4) and σ_{on} was calculated from Eq. (3).

4.2.2 Orifice Calibration

Determination of the conductance of the orifice was made using the steady-state pressures. Since $\frac{dP}{dt} = 0$, then Eq. (1) reduces to

$$P \frac{dV}{dt} = Q_1 + \zeta \quad (5)$$

For this chamber, at the higher leak rates, $\zeta \ll Q_1$, so that the outgassing may be ignored during calibration of the orifice. Thus,

$$P_c K - P_o K = P_f k$$

where K is the orifice conductance

$$\text{and} \quad K = \frac{P_f k}{(P_c - P_o)}$$

Using the calibration factors already determined for the gages, then

$$K = \frac{P_f k}{(\sigma_{cn} P_{cn} - \sigma_{on} P_{on})}$$

SECTION V EXPERIMENTAL RESULTS

5.1 EVALUATION OF GASES BY PUMPDOWN METHOD

These tests were carried out to determine the best gas for use in later quantitative tests. Figure 3 shows typical normalized He pumpdown curves for N_2 , O_2 , and Ar at an approximate flow rate of 5×10^{-2} torr-liters/sec measured at 300°K (approximate He partial pressure, 5×10^{-6} torr). As can be seen from the curves, N_2 is the least effective. Although O_2 seems to be as effective as Ar, problems of gage stability, particularly of the mass spectrometer, precluded any extensive testing with O_2 . The maximum He pumping speed, for the 7-in.-diam sphere, shown in these tests at 4.4°K is 6.7 liters/sec by Ar or O_2 and 4.7 liters/sec by N_2 .

TABLE I
RESULTS OF STEADY-STATE SORPTION TESTS

Flow Rate, torr-liters/sec		Partial Pressure, torr		Pumping Speed of 7-in. Sphere, liters/sec	Effective Capture Coefficient
Helium	Argon	Helium	Argon	Helium	Helium
1.79 x 10 ⁻⁴	-	2.12 x 10 ⁻⁶	-	Pumping by Orifice	$\left\{ \begin{array}{l} 84.4 \\ 84.3 \\ 83.7 \\ 84.4 \end{array} \right.$
3.58 x 10 ⁻⁴	-	4.25 x 10 ⁻⁶	-		
8.95 x 10 ⁻⁴	-	1.07 x 10 ⁻⁵	-		
1.79 x 10 ⁻³	-	2.12 x 10 ⁻⁵	-		
1.70 x 10 ⁻⁴	2.58 x 10 ⁻³	9.24 x 10 ⁻⁷	2.67 x 10 ⁻⁷	184.0	0.003
1.77 x 10 ⁻⁴	2.58 x 10 ⁻³	9.22 x 10 ⁻⁷	2.67 x 10 ⁻⁷	192.0	0.004
1.79 x 10 ⁻⁴	3.22 x 10 ⁻³	3.72 x 10 ⁻⁷	3.33 x 10 ⁻⁷	481.0	0.013
1.70 x 10 ⁻⁴	4.99 x 10 ⁻³	1.71 x 10 ⁻⁷	5.16 x 10 ⁻⁷	994.0	0.030
1.77 x 10 ⁻⁴	4.99 x 10 ⁻³	1.54 x 10 ⁻⁷	5.16 x 10 ⁻⁷	1,150.0	0.036
1.79 x 10 ⁻⁴	6.44 x 10 ⁻³	4.25 x 10 ⁻⁸	6.66 x 10 ⁻⁷	4,210.0	0.138
1.77 x 10 ⁻⁴	9.65 x 10 ⁻³	1.49 x 10 ⁻⁸	9.99 x 10 ⁻⁷	11,880.0	0.39
1.79 x 10 ⁻⁴	1.61 x 10 ⁻²	1.06 x 10 ⁻⁸	1.67 x 10 ⁻⁶	16,880.0	0.56
3.58 x 10 ⁻⁴	3.22 x 10 ⁻³	2.52 x 10 ⁻⁶	3.33 x 10 ⁻⁷	142.0	0.002
3.54 x 10 ⁻⁴	5.95 x 10 ⁻³	6.90 x 10 ⁻⁷	6.16 x 10 ⁻⁷	574.0	0.016
3.49 x 10 ⁻⁴	1.61 x 10 ⁻²	4.24 x 10 ⁻⁸	1.67 x 10 ⁻⁶	8,220.0	0.27
3.58 x 10 ⁻⁴	1.61 x 10 ⁻²	2.12 x 10 ⁻⁸	1.67 x 10 ⁻⁶	16,900.0	0.56
3.58 x 10 ⁻⁴	3.22 x 10 ⁻²	1.77 x 10 ⁻⁸	3.33 x 10 ⁻⁶	20,250.0	0.67
6.26 x 10 ⁻⁴	1.60 x 10 ⁻²	4.06 x 10 ⁻⁸	1.66 x 10 ⁻⁶	15,400.0	0.51
6.26 x 10 ⁻⁴	3.17 x 10 ⁻²	3.54 x 10 ⁻⁸	3.28 x 10 ⁻⁶	17,700.0	0.59
8.95 x 10 ⁻⁴	3.22 x 10 ⁻³	7.54 x 10 ⁻⁶	3.33 x 10 ⁻⁷	119.0	0.001
8.95 x 10 ⁻⁴	1.59 x 10 ⁻²	6.13 x 10 ⁻⁷	1.65 x 10 ⁻⁶	1,460.0	0.020
9.85 x 10 ⁻⁴	1.61 x 10 ⁻²	2.30 x 10 ⁻⁷	1.67 x 10 ⁻⁶	4,280.0	0.139
8.95 x 10 ⁻⁴	3.22 x 10 ⁻²	6.75 x 10 ⁻⁸	3.33 x 10 ⁻⁶	13,270.0	0.44
8.95 x 10 ⁻⁴	4.82 x 10 ⁻²	5.34 x 10 ⁻⁸	4.99 x 10 ⁻⁶	16,750.0	0.55
8.95 x 10 ⁻⁴	6.30 x 10 ⁻²	5.03 x 10 ⁻⁸	6.52 x 10 ⁻⁶	17,800.0	0.59
1.34 x 10 ⁻³	3.22 x 10 ⁻²	7.8 x 10 ⁻⁸	3.33 x 10 ⁻⁶	17,200.0	0.57
1.34 x 10 ⁻³	3.22 x 10 ⁻²	1.24 x 10 ⁻⁷	3.33 x 10 ⁻⁶	10,800.0*	0.36
1.79 x 10 ⁻³	3.22 x 10 ⁻²	2.38 x 10 ⁻⁷	3.33 x 10 ⁻⁶	7,520.0	0.22
1.79 x 10 ⁻³	6.30 x 10 ⁻²	1.10 x 10 ⁻⁷	6.52 x 10 ⁻⁶	16,270.0	0.54
2.68 x 10 ⁻³	3.21 x 10 ⁻²	1.48 x 10 ⁻⁶	3.23 x 10 ⁻⁶	1,810.0	0.06
2.68 x 10 ⁻³	6.28 x 10 ⁻²	1.65 x 10 ⁻⁷	6.50 x 10 ⁻⁶	16,220.0*	0.54
2.68 x 10 ⁻³	6.28 x 10 ⁻²	5.30 x 10 ⁻⁷	6.61 x 10 ⁻⁶	5,060.0*	0.15
3.58 x 10 ⁻³	6.28 x 10 ⁻²	2.31 x 10 ⁻⁷	6.50 x 10 ⁻⁶	15,500.0	0.51
4.46 x 10 ⁻³	6.24 x 10 ⁻²	2.92 x 10 ⁻⁷	6.45 x 10 ⁻⁶	15,270.0	0.50

*These values reflect the sensitivity of the sorption phenomena to slight temperature changes.

5.2 STEADY-STATE MEASUREMENTS

Table I is a summary of the reduced data obtained from these tests. The flow rates are given in torr-liters/sec at 300°K. Pumping speeds were obtained by dividing the input flow rate of He by the steady-state partial pressure of He. Figure 4 shows the He pumping speed as a function of the Ar/He ratio. It is apparent that the pumping speed increases with Ar pressure as well as with the Ar/He ratio. To increase our understanding of this relationship measurement of the adsorption isotherms of He on solid Ar were carried out.

5.3 ADSORPTION ISOTHERMS

The equilibrium pressure of He on a solid Ar substrate at 4.2°K was measured for several thicknesses of Ar deposit over a range of He/Ar ratios. A typical pressure-time trace is shown in Fig. 5. The results are shown in Figs. 6 and 7 where the He equilibrium pressure is plotted against the amount of He added and against the He/Ar ratio, respectively. For the amounts of Ar deposited, the He partial pressure is an exponential function of the He/Ar Ratio.

5.4 CAPTURE COEFFICIENTS

During deposition of the sorbent gases, the partial pressures of these substrate gases were recorded. From these data it was determined that the capture coefficients of N₂, Ar, and O₂ were all within the range from 0.97 to 0.99 for 77°K gas on a 4.2 to 4.5°K surface. The initial capture coefficient of He on a pure Ar substrate was found to be 0.53 ± 0.03 for 77°K He on 4.2°K Ar (Section 3.3).

SECTION VI DISCUSSION

Prior to the start of this experimental program certain theoretical calculations had indicated the feasibility of trapping as a means of pumping He. The calculations were based in part on the results of work on the trapping of N₂ by water cryodeposit (Ref. 5). In brief (see Appendix II), the heat of adsorption can be approximated by the geometric mean of the heats of evaporation of the two components. Furthermore, the heat of evaporation can be used to estimate the equilibrium pressure of the adsorbed gas at low surface coverage. For the systems He/N₂, He/O₂, and He/Ar, the calculated heats of adsorption and equilibrium pressures are tabulated below.

In addition to the foregoing, the free volumes of the cryodeposits were calculated. The reasoning behind this was that there should be enough free volume to accommodate He atoms, but that too large a free volume would allow rapid diffusion of the He from the surface. This is based upon the particular theory that, in trapping, the molecules captured are those that remain on the surface for a long enough time that they are covered over by the cryodeposit (Ref. 6). As can be seen from the table, there is little difference in the free volumes for the three substrate gases. All are large enough for rapid diffusion of He atoms.*

There are, however, appreciable differences in both the estimated heats of adsorption and in the estimated equilibrium pressures. From these pressures it was decided that trapping offered a good possibility for pumping of He and tentatively, that O₂ would probably be the best trapping substrate. In addition, it was noted that if the estimates of the heats of adsorption were correct, trapping of He would be extremely temperature sensitive (Ref. 7). At 4.2°K an increase of 0.1 degree in the surface temperature of Ar should lead to an increase of He pressure by a factor of 90.

Results of Some Calculations on Helium Sorption (see Appendix II)			
	He/N ₂	He/O ₂	He/A
Heat of Adsorption (cal/mole)	168	189	175
Monolayer Pressure (torr)	1.1×10^{-5}	8.7×10^{-7}	4.2×10^{-6}
Percent Free Volume of Substrate	39	43	43

6.1 PUMPDOWN TESTS

In a few preliminary tests, not reported here, this temperature sensitivity was confirmed (Refs. 8 and 9). Trapping was barely detectable (less than 0.05 liters/sec) above 4.5°K. However, below 4.5°K the

*The capacity of the lattice is about one He atom for every two molecules of substrate gas with a diffusion rate, estimated from classical mechanics, of about 2×10^{-3} torr-liter/cm²-sec at saturation (see Appendix II).

pumping speed increased as the temperature fell until at 4.4°K it reached about 5 to 7 liters/sec as calculated from the pumpdown curves (Fig. 3).

From these results and the theoretical correlation, it was seen that lower temperatures were necessary to achieve practical pumping rates. With full LHe recirculation, in the initial system, the lowest temperature possible was about 4.4°K, and the test times at constant temperature were of the order of from 10 to 15 min. Therefore, the LHe transfer system was reworked and an LHe flow control valve was installed as described in Section II. With this system, the cryosurface temperature could be held constant ($\pm 0.008^\circ\text{K}$) in the range from 4.18 to 4.22°K, depending on the barometric pressure. Test times up to 3 hr were obtained.

Since Ar and O₂ had shown similar results on the pumpdown tests (Fig. 3) the final choice of a substrate gas for quantitative testing was based on other considerations. The major consideration was the instability of the mass spectrometer in the presence of O₂ as compared to Ar. This factor overrode the expected larger increase in He pumping speed with O₂ for the same decrease of cryosurface temperature. Therefore, Ar was used for the steady-state tests.

A word of explanation is in order here. Although any well-defined test can, in principle, be made quantitative, in practice steady-state tests offer certain advantages. The response times of the various parts of a complex system can be ignored when the pressure is constant. More important, however, the pressure readings may be referred to any arbitrary temperature so that thermal transpiration corrections cancel out when one uses the temperature at which the gages were calibrated (Ref. 10). This is very helpful when the pressure gage receives molecules from surfaces at different temperatures, as is the case with the external gage in the present system. This is why, although the gas temperature was 77°K, all pumping speeds are reported in liters/sec at 300°K.

6.2 STEADY-STATE TESTS

The results of the steady-state tests are summarized in Table I (page 8). The theoretical impingement rate for the cryosphere is 30,000 liters/sec (adjusted to 300°K). Some of the pumping speeds shown in Table I indicate that better than one-half the He atoms striking the surface are pumped. This compares favorably with the Ho coefficient (Ref. 4) of from 0.3 to 0.4 for untrapped diffusion pumps.

Examining Table I more closely we see that the He pumping speed increases both with the Ar/He ratio and with the partial pressure of Ar. However, the relationship is complex and has not yet been resolved. Figure 4 shows the pumping speed as a function of the Ar/He steady-state pressure ratio.

The observed scatter in Fig. 4 is believed to be caused by the different Ar condensation rates and to slight day-to-day temperature variations of the cryosphere as described previously. (These tests were run on four separate days.) Another source of scatter is that a steady state was apparently not achieved in all cases even though a constraint of 5 min of constant pressure was imposed. The inadequacy of this constraint became obvious when the isotherm measurements were carried out.

6.3 ISOTHERM MEASUREMENTS

Figure 6 shows the equilibrium pressures obtained when He was added intermittently, in the presence of an existing cryodeposit of Ar, for four different amounts of Ar. These curves are all part of the same family. Figure 7 shows the same pressures plotted against the He/Ar mole ratio. This latter plot almost reduces the data to a single curve. The remaining scatter may be caused by a small uncertainty in the amount of Ar added.

If the surface were nonporous the pressure would be dependent only on the amount of He added which, however, is not the case as illustrated in Fig. 6. Rather, Fig. 7 indicates that the surface area available for He sorption is proportional to the total Ar added. This suggests that either the deposit is porous or that the He diffuses rapidly through the solid as was proposed earlier in this discussion. If the former is the case, then the isotherms should fit one of the adsorption equations. However, if it is a matter of solubility, the pressures should follow Henry's law at low concentrations. Henry's law predicts a linear relationship between concentration and pressure (Ref. 7). These results show an exponential dependence of pressure on the mole ratio so that solution of He in the solid Ar seems an unlikely mechanism. Neither do the data match the Langmuir (nor BET) isotherms at these pressures (Ref. 11). Agreement can be obtained with the mobile monolayer equation (Ref. 7) for adsorption but at this point there arises a question which cannot be answered from the available data. Is there justification for applying classical adsorption theories to these results when it is well

known that He shows large quantum effects* in this temperature range? The fact that the plot of log vapor pressure versus reciprocal temperature has the "wrong" curvature indicates that quantum corrections are not negligible (Ref. 12). Thus, our present tests are insufficient to determine the mechanism of He sorption.

The isotherm measurements do show, however, that when one deposits He and Ar at one ratio and then changes the ratio, one can expect the two layers to interact. The apparent dependence of sorption area on the total Ar deposit indicates that He diffuses into the Ar by some mechanism. Thus, it would be able to diffuse from a more concentrated layer to a more dilute layer. The time required would depend on the value of the condensation rate relative to the diffusion rate. Thus, when the Ar/He ratio is changed the pressure would depend on both the concentration gradient through the substrate and that in the surface. When these are equal the pressure becomes constant for a time. The true steady-state pressure would not be reached, however, until both gradients become zero. If the change in the Ar/He ratio is discontinuous, this would lead to the pressure falling or rising in a stepwise fashion. Such behavior was, in fact, observed in some of the steady-state tests when many measurements had been taken sequentially over a range of flow ratios.

The maximum error from this psuedo-steady-state pressure is estimated to be 20 percent. This is larger than the 5-percent total calibration error but smaller than the twofold deviation which can arise from temperature differences. The latter unfortunately cannot be particularized because part of the refrigeration He was vented to atmosphere and part was recycled in these tests.

6.4 FUTURE WORK

The results of these tests indicate that not only does trapping offer a practical alternative to diffusion pumping of He but also that this work presents a unique opportunity for improving the understanding of sorption phenomena in general by extending sorption studies to the range where interaction between adsorbed molecules can be neglected. Isotherm measurements at different temperatures will give the heats of adsorption.

*At low temperatures the difference between quantum and classical statistics is no longer negligible.

At very low surface coverage, this would give information pertinent to the problem of estimating the intermolecular potential between unlike molecules.

However, it will be necessary to shed some light on the problem of quantum corrections. One approach would be to raise the chamber pressure to the point where two-dimensional, surface condensation occurs. If condensation can be demonstrated then the hypothesis of the mobile monolayer is confirmed, and the quantum corrections for sorption will parallel those for the gas phase. If surface condensation cannot be shown then it may be necessary to test He of atomic weight three in order to sort out the quantum corrections from other effects.

Plans have been made to modify the chamber to obtain a controlled cryosurface temperature over the range from 3.5 to 5°K. A further change will involve using a different mass spectrometer which has been found to be stable in the presence of O₂.

With these modifications a complete study of He sorption on various solidified gas substrates becomes possible. It is expected that measurements over a range of temperatures for different gases will lead to substantial contributions to the theory of adsorption. This will be in addition to the practical purpose of additional tests to further explore and optimize this method of He pumping.

SECTION VII CONCLUSIONS

A method for pumping He which compares favorably in pumping speed with that available from diffusion pumps has been demonstrated. This method should prove useful for small chambers. For large chambers the high cost of LHe will have to be balanced against the desirability of having an absolutely oil-free system. In addition to the practical importance of this development, the capture probability (0.67 max) is sufficiently high that new understanding of both adsorption phenomena and of the interaction energy between unlike molecules becomes possible.

Future experiments will be directed to a study of He sorption by various condensed gases, over a range of temperatures (from 3.5 to 5.0°K) for optimization of this pumping method and for application to the theory of sorption.

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APPENDIX I
ILLUSTRATIONS

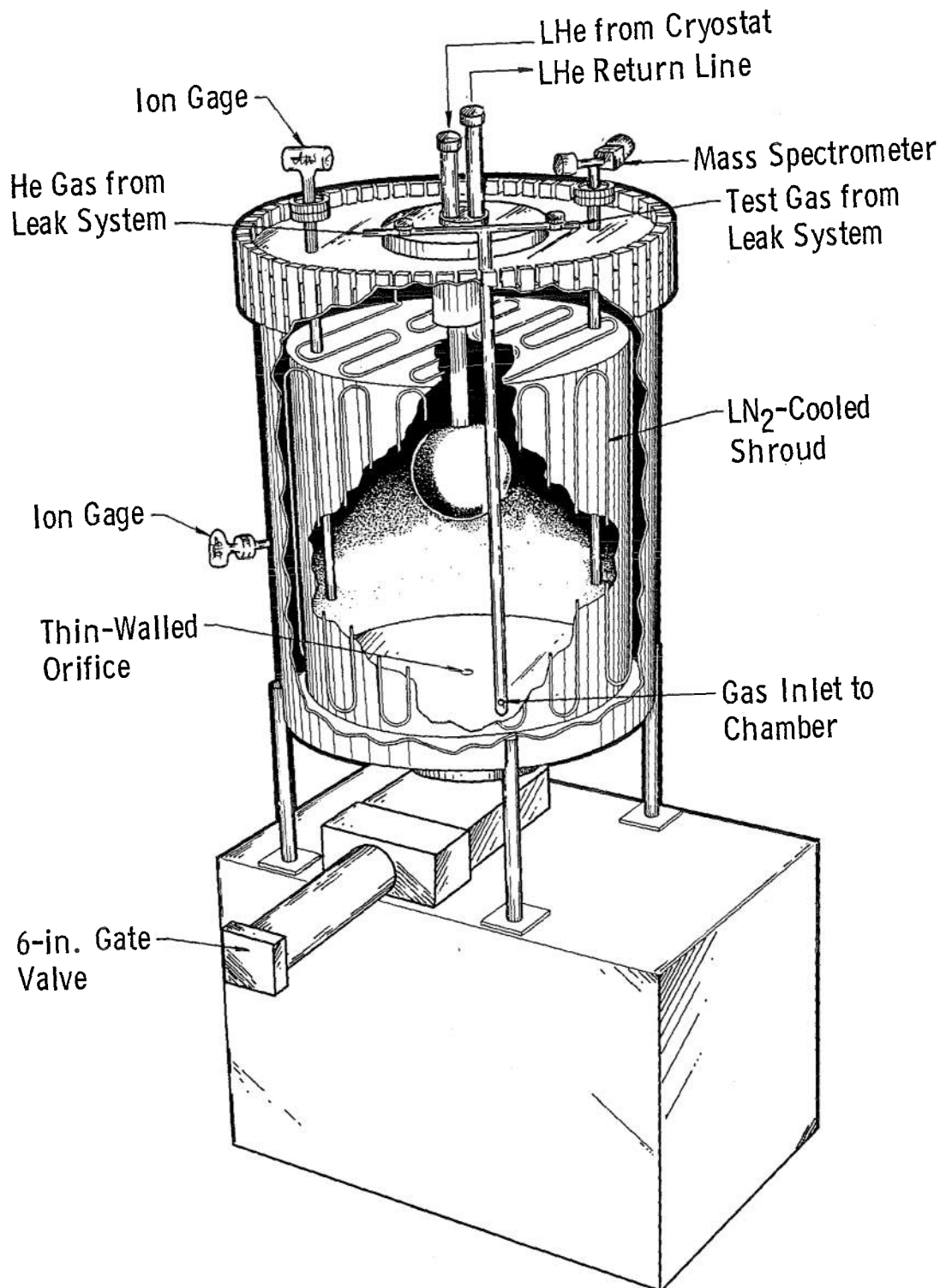


Fig. 1 UHV Chamber

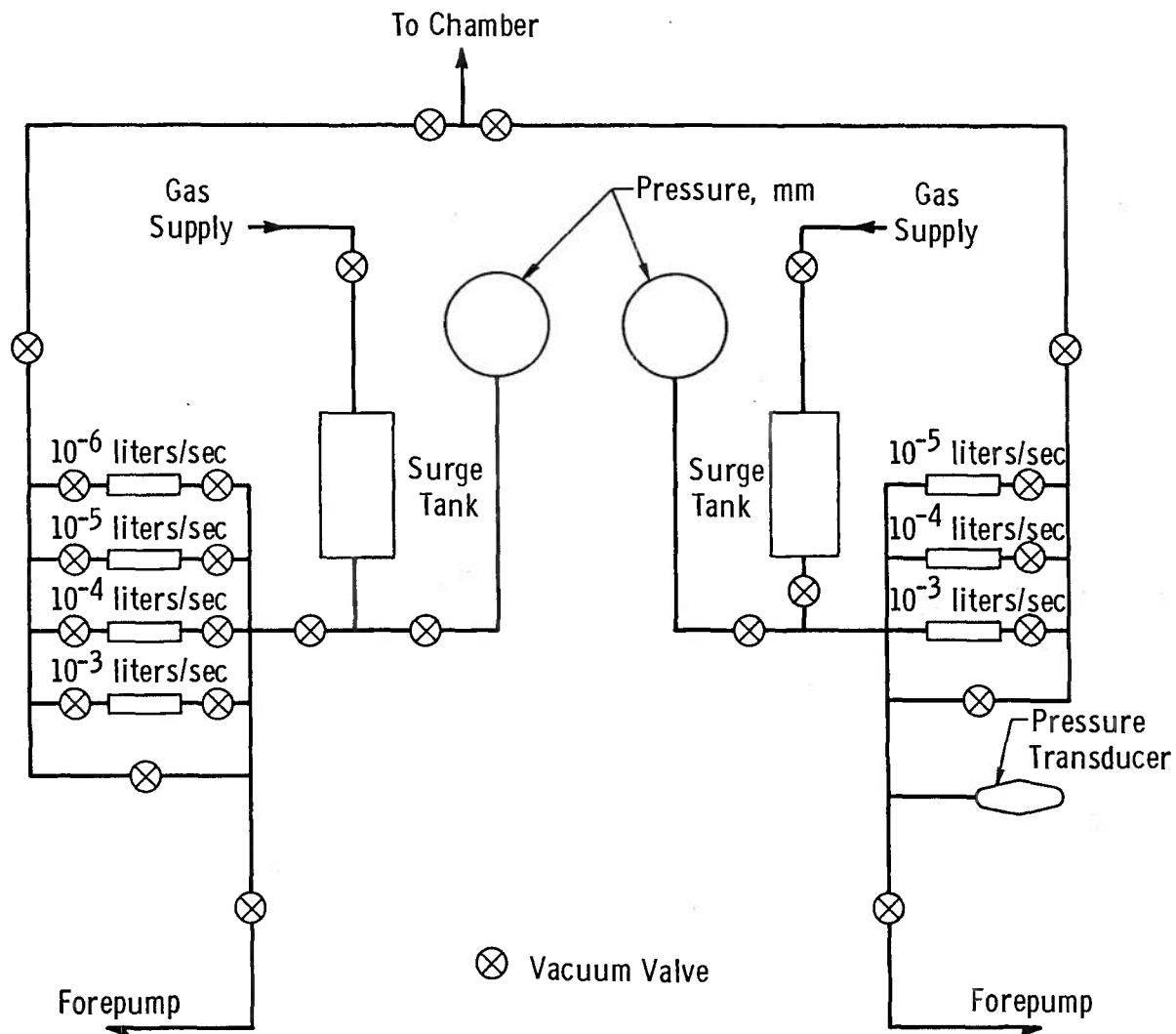


Fig. 2 Gas Addition System

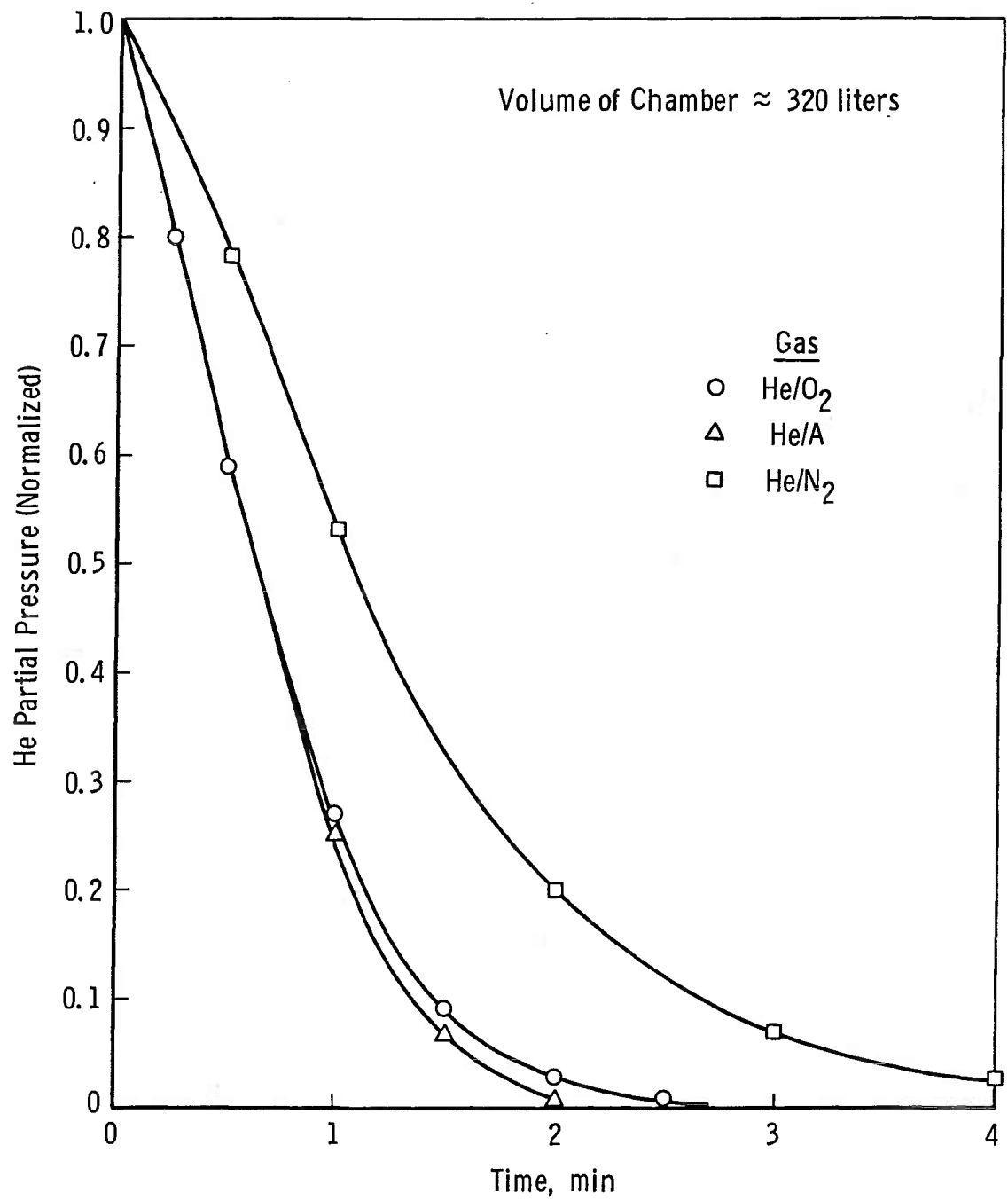


Fig. 3 Typical Pumpdown Curve

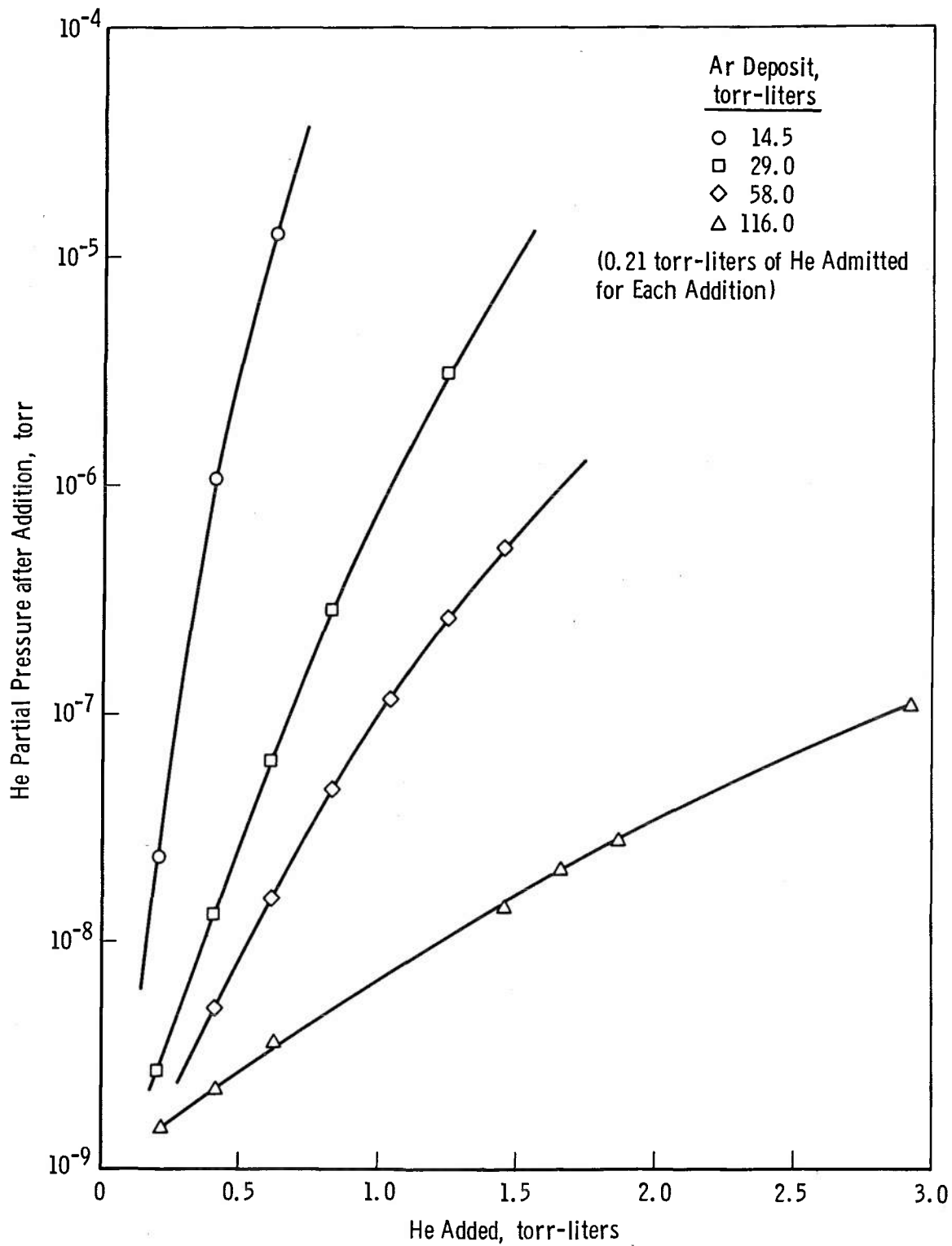


Fig. 6 Helium/Argon Pressure Isotherm

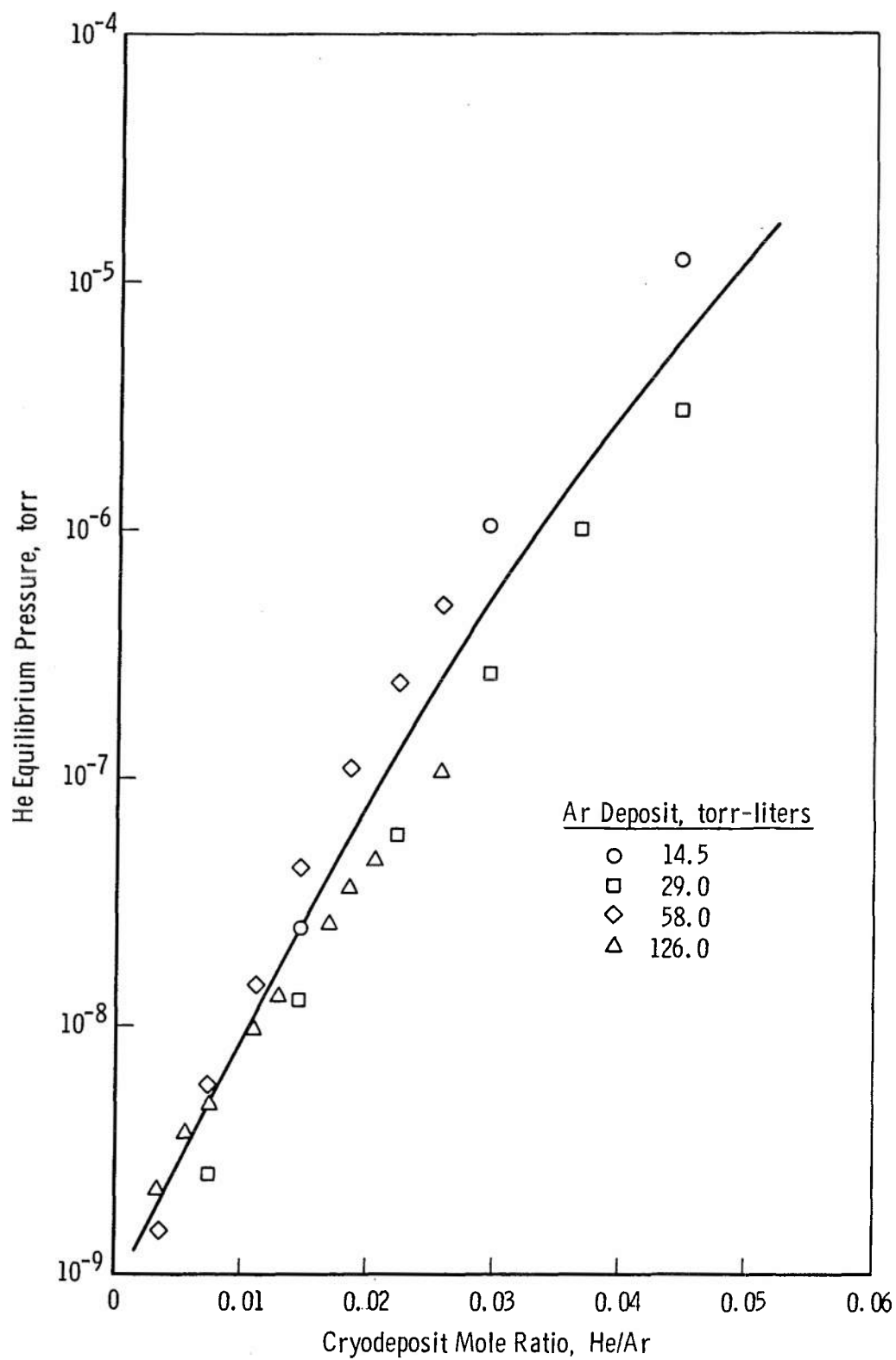


Fig. 7 Helium Isotherm versus Mole Ratio Helium/Argon

APPENDIX II
METHODS OF CALCULATIONS

METHODS OF CALCULATIONS

Certain speculative calculations were carried out prior to the initiation of experimental work. These were lacking in rigor and highly intuitive, intended only to estimate the probability of success of the subsequent tests. The details of these calculations are reported here.

HEAT OF ADSORPTION

The heats of adsorption are assumed to be equal to the geometric mean of the heats of evaporation of the sorbate and sorbent gases. Some justification for this is that in Ref. 1 the heat of sorption (erroneously referred to as ΔF) of GN_2 by ice at 77°K was found to be 3260 ± 910 cal/mole. The geometric mean of the heats of vaporization of H_2O and N_2 is 4040 cal/mole, which is in agreement within the experimental error limits.

MONOLAYER PRESSURE

From thermodynamics, the following relationship may be derived between the vapor pressure and the heat of evaporation which is valid when the vapor density is much less than the density of the condensed phase.

$$P_v = P^\circ \exp - \frac{\Delta H_v}{RT} \quad (\text{II-1})$$

where

P_v = vapor pressure

ΔH_v = heat of evaporation

R = universal gas constant

T = absolute temperature

P° = constant

By the same reasoning, the sorption pressure and heat of sorption may be substituted in this equation. If it is assumed that the entropy of the condensed phase is the same for desorption and evaporation, then the constant P° will be the same for vapor pressure and for sorption pressure. Thus

$$P_a = P^\circ \exp - \frac{\Delta H_a}{RT} \quad (\text{II-2})$$

Combining Eqs. (II-1) and (II-2)

$$P_a = P_v \exp - \frac{\Delta H_a - \Delta H_v}{RT} \quad (\text{II-3})$$

Based on these assumptions the equilibrium pressure at low surface concentration may be calculated from Eq. (II-3). Since the surface concentration of the adsorbed molecules is not specified, Eq. (II-3) should only be used qualitatively to estimate probabilities as in Section VI of this report.

FREE VOLUME

The free volume in a condensed phase may be estimated from the density and the molecular radius. Because the molecular radius is not a definite value but depends on the method of measurement, the molecules are assumed to be spherical. The total volume of a mole is given by

$$V = \frac{M}{\rho}$$

where M is the molecular weight and ρ is the density. The occupied volume is the number of molecules times the volume of a molecule, or

$$v = N \frac{\pi d^3}{6}$$

where

d = the molecular diameter (Van der Waals) (Ref. 13)

N = Avogadro's number, 6.023×10^{23}

Therefore, the free volume is given by

$$v_f = V - v$$

The volume available for an He atom within the solid may be estimated by assuming a geometric structure of the solid. If hexagonal packing is assumed, the edge length (ℓ) of a 60-deg parallelopiped made up of eight Ar atoms may be calculated from the density of solid Ar (1.65 gm/cc) (Ref. 13).

$$V = \frac{\sqrt{2} \ell^3}{2}$$

Since each corner is shared with eight other parallelopipeds, this is the volume associated with each Ar atom. Multiplying by Avogadro's number, the volume per mole is obtained. Thus,

$$\sqrt{2} N \frac{\ell^3}{2} = \frac{M}{\rho}$$

rearranging

$$\ell^3 = \frac{\sqrt{2} M}{\rho N} = 56.95 \times 10^{-24} \text{ cc}$$

and

$$\ell = 3.85 \times 10^{-8} \text{ cm}$$

The parallelopiped consists geometrically of two tetrahedra and an octahedron. The maximum sphere radius, tangent to the Ar spheres is 0.88×10^{-8} cm in the tetrahedra and 1.25×10^{-8} cm in the octahedron. The Van der Waals radius of an He atom is 1.35×10^{-8} cm (Ref. 13). A slight deformation of the parallelopiped is necessary to contain an He atom. From these results it is concluded that the capacity of the solid Ar lattice for He is such that between one and two Ar atoms will be required to contain one He atom at saturation.

HELIUM DIFFUSION RATE

Eyring's (Ref. 14) model of diffusion in the liquid state and Zener's model (Ref. 15) for the solid state lead to very similar equations and yield almost the same value for the diffusion constant of He in solid Ar. We will follow the treatment attributable to Eyring.

$$D = \frac{\lambda^2}{V_f^{1/3}} \sqrt{\frac{RT}{2\pi M}} \exp - E/RT$$

In this equation

D = diffusion constant, cm^2/sec

λ = distance diffusing particle travels in one step, cm

V_f = the free volume in the lattice, $\text{cm}^3/\text{molecule}$

$\sqrt{\frac{RT}{2\pi M}}$ = the incidence rate of molecules on a surface, cm/sec

E = the heat of evaporation, cal/mole

The heat of evaporation for He from an Ar lattice would be the same as the heat of adsorption already calculated and the distance per step is the same as the distance between Ar atoms. Substituting in the above equation

$$D = \frac{(3.85^2 \times 10^{-16}) (3.74 \times 10^3)}{(9.9) 6.023 \times 10^{23}} \exp - \frac{175}{1.987 \times 4.22}$$

$$D = 1.96 \times 10^{-13} \text{ cm}^2/\text{sec}$$

The diffusion rate in one dimension is given by

$$\frac{dc}{dt} = D \frac{dc}{dx}$$

Consider now a nearly saturated Ar lattice with one He for each two Ar atoms. The concentration, c , of He will be

$$c = \frac{\rho}{2M} = \frac{1.65}{2 \times 40} = 2.06 \times 10^{-2} \text{ mole/cc}$$

At the lattice surface this concentration drops to almost zero in the gas phase within a distance of one lattice edge length. Thus:

$$\frac{dc}{dx} = \frac{2.06 \times 10^{-2}}{3.85 \times 10^{-8}} = 5.35 \times 10^5 \text{ mole/cm}^4$$

and

$$D \frac{dc}{dx} = 1.96 \times 10^{-13} \times 5.35 \times 10^5 = 1.05 \times 10^{-7} \text{ mole/cm}^2\text{-sec}$$

$$= 1.96 \times 10^{-3} \text{ torr-liters/cm}^2\text{-sec (300°K)}$$

For this rate of evolution of He from the saturated Ar a pressure of He in the gas phase of at least 7.3×10^{-6} torr would be required to give an equal rate of sorption.

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1. ORIGINATING ACTIVITY (Corporate author) Arnold Engineering Development Center ARO, Inc. Operating Contractor Arnold Air Force Station, Tennessee		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
		2b. GROUP N/A
3. REPORT TITLE HELIUM PUMPING BY 4.2 ⁰ K CRYODEPOSITS		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) N/A		
5. AUTHOR(S) (Last name, first name, initial) Haygood, J. D. and Dawbarn, R., ARO, Inc.		
6. REPORT DATE January 1967	7a. TOTAL NO. OF PAGES 38	7b. NO. OF REFS 15
8a. CONTRACT OR GRANT NO. AF 40(600)-1200	9a. ORIGINATOR'S REPORT NUMBER(S) AEDC-TR-66-204	
b. Program Element 65402234		
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.	N/A	
10. AVAILABILITY/LIMITATION NOTICES Distribution of this document is unlimited.		
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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
2 cryopumping Helium 2 cryodeposits vacuum pumping space simulation argon sorption <i>1. Helium</i> <i>4 Argon</i> <i>Cryopumping</i> <i>19-2</i>						

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